

Generalizing Planck's distribution by using the Carati-Galgani model of molecular collisions

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Abstract

Classical systems of coupled harmonic oscillators are studied using the Carati-Galgani model. We investigate the consequences for Einstein's conjecture by considering that the exchanges of energy, in molecular collisions, follows the Lévy type statistics. We develop a generalization of Planck's distribution admitting that there are analogous relations in the equilibrium quantum statistical mechanics of the relations found using the nonequilibrium classical statistical mechanics approach. The generalization of Planck's law based on the nonextensive statistical mechanics formalism is compatible with the our analysis.

Key words:

Planck's law, nonequilibrium, superstatistics

1 Introduction

It was observed that for blackbody radiation[1] the mean energy U of stationary electromagnetic waves is a function of frequency ν of these waves: at

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temperature T we can write

$$U(\nu \rightarrow 0) \rightarrow k_B T \quad \text{and} \quad U(\nu \rightarrow \infty) \rightarrow 0, \quad (1)$$

where k_B is the Boltzmann constant. This contradicts the energy equipartition law of classical statistical mechanics in that U is frequency independent. The important contribution of Planck came when he discovered that one could obtain the experimental result of Eq. (1) by treating the energy of the stationary electromagnetic waves as a discrete spectra. Planck's law opened the way for quantum mechanics.

In such a way, Einstein [2] gave an important contribution by noticing that in the canonical ensemble the fluctuation of energy of the blackbody radiation is compatible with Planck's law when it is, in terms of its variance σ_E , expressed in terms of the mean energy U through the relations

$$\frac{dU}{d\beta} = -(\sigma_E)^2 \quad (2)$$

and

$$(\sigma_E)^2 = \epsilon U + \frac{U^2}{N} \quad (3)$$

where $\beta = 1/(k_B T)$, $\epsilon = h\nu$ (h is Planck's constant) and N is the number of quantum particles. Einstein imagined the first relation as being exactly a type of general thermodynamic relation, while the second must have a dynamical character, being, in principle, deducible from a microscopic dynamics.

Recently, Carati and Galgani [3,4] have investigated classical systems of coupled harmonic oscillators with the procedure of Jeans-Landau-Teller dynamic of molecular collisions [5,6]. The principal results of Carati-Galgani are that: i) relaxation times to equilibrium are nonuniform and depend on the internal degrees of freedom of the considered system; ii) Situations of nonequilibrium statistical mechanics very far from equilibrium are described, in a first order approximation, by the analogous relations found in quantum equilibrium statistical mechanics; iii) as conjectured by Einstein, Eq. (3) is a consequence of the dynamics.

It is important to remark that Planck's law considers a real equilibrium state of the quantum statistical mechanics, while within the framework of Carati-Galgani, a similar relation to Planck's law was obtained using nonequilibrium classical statistical mechanics.

The purpose of the present work is to study classical systems of coupled harmonic oscillators along the line of Carati-Galgani. We studied three different aspects of this framework. First, we analyzed the consequence for Einstein's conjecture by assuming that the exchanges of energy, in molecular collisions, follows the Lévy type statistic for high enough frequencies. The Lévy statistics for the energy exchanges was recently obtained by Carati et al. [7], considering the dynamics over a finite time in the Jeans-Landau-Teller model. Secondly, admitting that there are analogous relations in the equilibrium quantum statistical mechanics of the relations found here using the nonequilibrium classical statistical mechanics approach, we will explore some possible consequences in quantum radiation theory. Third, we show that the generalization of Planck's law [8] within the framework of the recently introduced superstatistic formalism [9,10] is compatible with the our analysis of Einstein's conjecture.

The organization of this paper is as follows. The Carati-Galgani model is briefly explained in Sec. II. Our generalization is presented in Sec. III. Discussions about the consequences of our results are presented in Sec. IV. Concluding remarks are given in Sec. V.

2 The Carati-Galgani model

A good level of interest has been focused on the problem of estimate energy exchanges between vibrational and translational degrees of freedom in the dynamic of molecular collisions. One of the simplest and main model used to study this problem was published by Carati and Galgani [3,4]. It is based on the Jeans-Landau-Teller approach [5]. A possible example of a physical system that reproduce this formalism follows.

Let us imagine a one-dimensional system involving two particles P and Q in a line. P is attracted by a linear spring to the fixed origin through a harmonic oscillator potential. Q interacts with P through an analytical potential. In a first approximation, the variation of energy δe in a simple collision between P and Q for the oscillator P of frequency ν is given by the addition of a drift term and others dependent on the fluctuation of the oscillator's initial phase. It is easy to show [3] that after t collisions an oscillator has energy

$$\epsilon_t = \epsilon_0 + t\eta^2 + 2\eta \sum_{j=1}^t \sqrt{e_{j-1}} \cos(\varphi_{j-1}). \quad (4)$$

ϵ_0 is the oscillator's initial energy that is considered to be very small in order that the motion of P and Q be decoupled. φ_j is the phase of the oscillator in the j th collision and η is evaluated as a function of ν , which is known to be

decreasing exponentially with ν (for an analysis of η see [6]).

Let us consider a assembly of oscillators, averaging over the phases φ_j , in order that

$$\langle \epsilon_t \rangle = \langle \epsilon_0 \rangle + t\eta^2 + 2\eta \sum_{j=1}^t \langle \sqrt{e_{j-1}} \cos(\varphi_{j-1}) \rangle. \quad (5)$$

where $\langle \dots \rangle$ is the phase average. Considering the phases to be independent and uniformly distributed, for large t , the average of energy and the variance are, respectively, given by

$$\langle \epsilon_t \rangle = \langle \epsilon_0 \rangle + t\eta^2 \quad (6)$$

and

$$\sigma_{\epsilon_t}^2 = 2\epsilon_0 \langle \mu_t \rangle + \langle \mu_t^2 \rangle. \quad (7)$$

Here $\sigma_{\epsilon_t}^2$ and $\langle \mu_t \rangle$ correspond to, respectively, the variance and mean of the exchanged energy $(\epsilon_t - \epsilon_0)$. Observe that the functional form of the variance is independent of t and η .

Assuming N independent identical oscillators and considering the total energy $\langle E_t \rangle = \sum_j \langle \mu_t^j \rangle$, we immediately obtain for the variance $\sigma_E^2 = N\sigma_{\epsilon}^2$ and mean $U = N\langle \mu \rangle$ of the exchanged energy

$$(\sigma_E)^2 = 2\varsigma\nu U + \frac{U^2}{N} \quad (8)$$

where ς is the initial action per oscillator [3]. This result represents essentially the application of the central limit theorem, that arise from a large number of independent contributions of the oscillators [11] .

Equation (8) is analogous to Einstein's relation obtained in the Bose-Einstein quantum statistical mechanics theory. Despite the fact that this relation has been obtained considering the classical statistical mechanics very far from equilibrium, the approach recovers Einstein's conjecture, i.e., proving it to be a consequence of the dynamics.

3 The generalization of the Einstein's conjecture

Recently, Carati et al. [7] showed that there are systems which present qualitative differences between the statistics obtained using the equilibrium distribution and that obtained through the dynamics over a finite time. Considering the dynamics over a finite time of the Jeans-Landau-Teller model, they obtained that the exchanges of energy follow the Lévy type statistics for high enough frequencies. An immediate consequence of this result, based on the Lévy flight random walk [13], is that $\langle \mu_t^2 \rangle$ is infinite.

We notice that in the Carati-Galgani model it is assumed that the oscillators have low energies and the collisions are separated from each other so that the oscillator phases are completely independent. Here, we must be able to answer what happens if the $\langle \mu_t^2 \rangle$ is not finite? In this way, we can no longer write Eq. (7) and, as consequence, Eq. (8) is not valid either.

It is well known that for $\langle \mu_t^2 \rangle \rightarrow \infty$ the theoretical basis is the Lindeberg-Lévy central limit theorem [14]. Since we are considering the case of low energies for the oscillators, using the same steps as were used to obtain Eq. (7), it is straightforwardly verified that

$$\sigma_\epsilon^2 = 2\epsilon_0 \langle \mu \rangle + \varepsilon^{(2-\alpha)} \langle \mu^\alpha \rangle \quad 1 \leq \alpha < 2, \quad (9)$$

where ε is a constant that has dimension of energy and is suitably chosen by dimensional requirements.

Finally, for N independent identical oscillators, we find

$$\sigma_E^2 = 2\zeta\nu U + \varepsilon^{(2-\alpha)} \frac{U^\alpha}{N^{\alpha-1}} \quad (10)$$

which generalizes the dynamic proposal of Einstein and will be our hypothesis to get the generalizations of Einstein's conjecture and Planck's law.

4 Possible relations in equilibrium statistical mechanics

Let us now explore the possibility of there existing analogous relations in the equilibrium quantum statistical mechanics of the relations found here using the nonequilibrium classical statistical mechanics approach.

We start the process using Eq. (2) in conformity to Einstein's vision. In this

case, using Eq. (10) in Eq. (2) we have

$$-\frac{dU}{d\beta} = 2\varsigma\nu U + \varepsilon^{(2-\alpha)} \frac{U^\alpha}{N^{\alpha-1}}. \quad (11)$$

It is straightforward to find the energy distribution

$$U = N \left\{ \frac{2\varsigma\nu}{\varepsilon^{(2-\alpha)} [e^{(\alpha-1)2\varsigma\nu\beta} - 1]} \right\}^{\frac{1}{\alpha-1}}, \quad (12)$$

in order that we can consistently rewrite Eq. (12) as

$$\tilde{U} = \frac{H\nu}{(e^{\beta H\nu/d} - 1)^d}. \quad (13)$$

We have introduced $\tilde{U} \equiv \frac{U z^{d-1}}{N}$, $H \equiv 2\varsigma$ and $d \equiv \frac{1}{\alpha-1}$ with $1 \leq d < \infty$. We assumed $\varepsilon \propto H\nu$ that leads to the expression $\varepsilon = zH\nu$ with z a pure dimensionless number. For $d = 1$, H coincides with Planck's constant h , and the U associated with Bose-Einstein quantum statistic is reobtained.

In the same way as the Planck blackbody radiation has its origin in the Bose-Einstein statistics, here obtained using $d = 1$, we can take other values of d , so that we can obtain new physical systems such that Eq. (13) may be applied. By following along standard lines, after straightforward calculations, the density of energy per unit volume is obtained as

$$\Omega_d(\nu) = g(\nu)U = \frac{8\pi H\nu^3}{z^{d-1}c^3 [e^{\beta H\nu/d} - 1]^d} \quad (14)$$

where we use the standard density of states of the photons ($g(\nu) = 8\pi\nu^2/c^3$). Fig. 1 presents $\Omega_d(\nu)$ versus energy $H\nu$ for typical values of d and $\beta = 1$. Note that if d increases then $\Omega_d(\nu)$ increases. Although $\Omega_3(0)$ has a finite value for $\nu \rightarrow 0$, it is null for $d < 3$ while it is infinity for $d > 3$ (see inset). The Ω_d is modified significantly when d varies. The Ω_d are illustrated in Figs. 2 and 3 for, respectively, $d = 2$ and $d = 4$ and various values of β . For d fix, we note small changes for Ω_d when β varies.

In the $H\nu\beta \ll 1$ regime

$$\Omega_d(\nu) \sim \frac{8\pi\nu^{3-d}}{(zH)^{d-1}c^3} (dK_B T)^d \quad (15)$$

which generalizes the Rayleigh-Jeans law. The generalization of Wien's law is

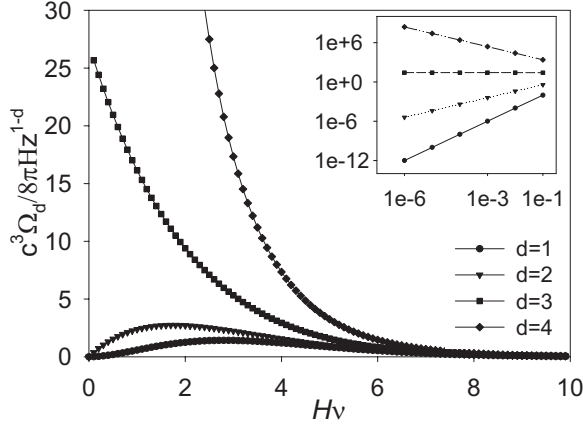


Fig. 1. The density of energy per unit volume versus energy for $d = 1, 2, 3, 4$ and $\beta = 1$. (Inset shows a closeup of part of the graph for $\nu \rightarrow 0$)

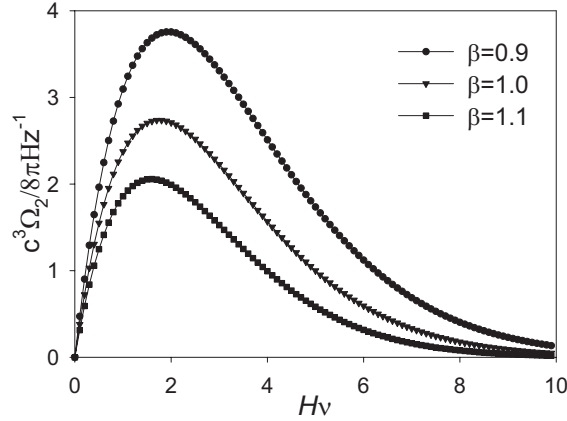


Fig. 2. The density of energy per unit volume versus energy for $\beta = 0.9, 1.0, 1.1$ and $d = 2$.

obtained in the $H\nu\beta \gg 1$ region

$$\Omega_d(\nu) \sim \frac{8\pi H\nu^3}{z^{d-1}c^3} e^{-\frac{H\nu}{k_B T}}, \quad (16)$$

and the Stefan-Boltzmann law for the total emitted power per unit surface is attained from the usual one, given by $j = \sigma_d T^4$, where the d -dependence is present only in the prefactor σ_d .

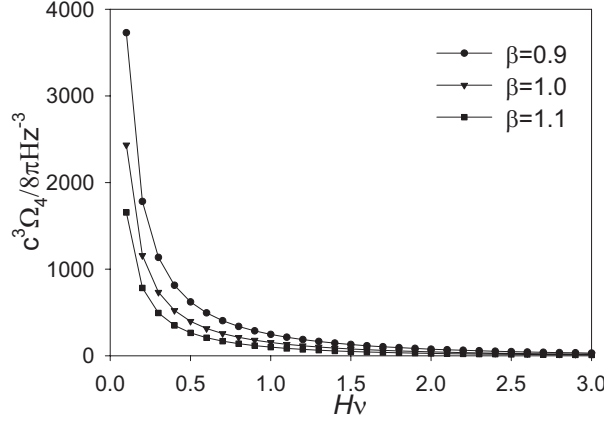


Fig. 3. The density of energy per unit volume versus energy for $\beta = 0.9, 1.0, 1.1$ and $d = 4$.

5 Souza-Tsallis generalization from the Einstein's conjecture

In fact, one of the characteristics of Eq. (13) is that it reproduces the results of Souza and Tsallis [8]. Observe that for $\tilde{U} = H\nu\bar{n}$ we can obtain the particle-number distribution

$$\bar{n} = \frac{1}{(e^{\beta H\nu/d} - 1)^d}. \quad (17)$$

Adopting the formal theory of statistical mechanics, it is straightforward to find the variance of an ensemble of n particles as being

$$\sigma_n^2 = \bar{n} + \bar{n}^\alpha \quad (18)$$

which generalizes the bosonic Landau's relation [15].

Ref. [8] obtained the Eqs. (17) and (18) heuristically based on the nonextensive statistical mechanics [16] and Beck-Cohen superstatistics [9,10]. They were based on the discussion of the differential equation $dy/dx = -a_1 y - (a_q - a_1) y^\alpha$ (with $y(0) = 1$), whose particular case $\alpha = 2$ corresponds to Bose-Einstein statistics. Our formalism describes the Souza-Tsallis generalization from the Einstein's dynamical fluctuation viewpoint.

Finally, we see that Eq. (17) can be written as

$$\bar{n} = \sum_{i=0}^{\infty} g(i, d) e^{-\beta E_i}, \quad (19)$$

where we obtain the energy spectrum

$$E_i(d) \equiv \frac{H\nu}{d}(i + d), \quad (20)$$

and its degeneracy

$$g(i, d) \equiv \frac{\Gamma(i + d)}{\Gamma(d)\Gamma(i + 1)}, \quad (21)$$

$\Gamma(x)$ being the gamma function. The spectrum is made of equidistant levels, like that of the quantum harmonic oscillator, with a constant energy difference between successive levels equal to $H\nu/d$.

6 Conclusions

Summarizing, we introduced a generalization of Einstein's conjecture considering an approach along the line of the Carati-Galgani model of molecular collisions. We obtained Planck's distribution compatible with the Beck-Cohen superstatistics. Furthermore, establishing a metaequilibrium very far from equilibrium for the system studied, and admitting that there are analogous relations in the equilibrium quantum mechanics, we generalized Planck's law.

For instance, the effects in the quantum radiation theory were obtained theoretically, as a first order approximation, of a classical system very far from equilibrium [4]. We emphasize that we are working with classical models of molecular collisions and not quantum models for blackbody radiation. Understanding the relationship between these two points of view is an open problem.

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